

# The Surface Diffusion Length of Water Molecules on Faceted Ice: A Reanalysis of “Roles of Surface/Volume Diffusion in the Growth Kinetics of Elementary Spiral Steps on Ice Basal Faces Grown from Water Vapor,” by Asakawa et al.

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**Abstract.** We reanalyzed the measurements made by Asakawa et al. [1] of the growth velocities of single-molecule-high steps on basal ice surfaces, as we believe the authors made a number of incorrect assumptions regarding ice growth parameters and bulk diffusion in their experiments. Applying what we believe are more accurate assumptions, we used the data in [1] to derive a surface diffusion length of  $x_s \approx 10$  nm for water molecules on basal ice surfaces at  $T = -8.4$  C, about 500 times lower than what was reported in [1]. Moreover, in our analysis we found that no information about the height of the Ehrlich-Schwoebel barrier could be obtained from these measurements.

## 1 Introduction

In [1], the authors describe a series of remarkable measurements of the growth velocities of single-molecule-high steps on a basal ice surface at  $T = -8.4$  C. Specifically, they measured the step velocity  $v_{step}$  for a series of what can be approximated as equally spaced steps, as a function of the spacing  $L$  between steps. They also measured  $v_{step}$  as a function of the water vapor supersaturation  $\sigma_{ref}$  at a ice-coated reference surface that served as a water vapor source. The experiments were conducted in air at normal atmospheric pressure.

In their analysis of these measurements, the authors found that the surface diffusion length for water molecules on a faceted basal surface was  $x_s \approx 5$   $\mu\text{m}$ , and they found that the attachment coefficient for water molecules on the basal surface near a step was  $\alpha \approx 10^{-5}$ . At low  $\sigma_{ref}$ , they measured the step kinetic coefficient (defined by  $v_{step} \approx \beta^L \sigma_{ref}$ ) was  $\beta^L \approx 700$   $\mu\text{m}/\text{sec}$ .

As described below, we believe that the authors substantially underestimated the effects of bulk diffusion (of water molecules through the air) in the analysis of their measurements. We also believe that the attachment coefficient  $\alpha \approx 10^{-5}$  they derived is strongly inconsistent with a number of other measurements that reported  $\alpha \approx 1$  for the same quantity. We therefore reanalyzed the data in [1] using what we believe is an improved treatment of bulk diffusion, along with more realistic assumptions regarding  $\alpha$ .

## 2 Diffusion Analysis

Consider the idealized experimental system shown in Figure 1, which is similar to that described in the data analysis section in [1] (specifically the analysis described in Equations 1 through 11 in [1]). We assume a constant supersaturation  $\sigma_{top}$  at the top surface of this simplified growth chamber (with the supersaturation being measured relative to the temperature of the bottom surface), and we assume that the bottom surface consists of a single faceted basal ice surface containing a series of one-molecule-high steps with spacing  $L$ . As in [1], the step velocity can be written

$$v_{step} = \frac{L}{a} \langle v_{basal} \rangle \quad (1)$$

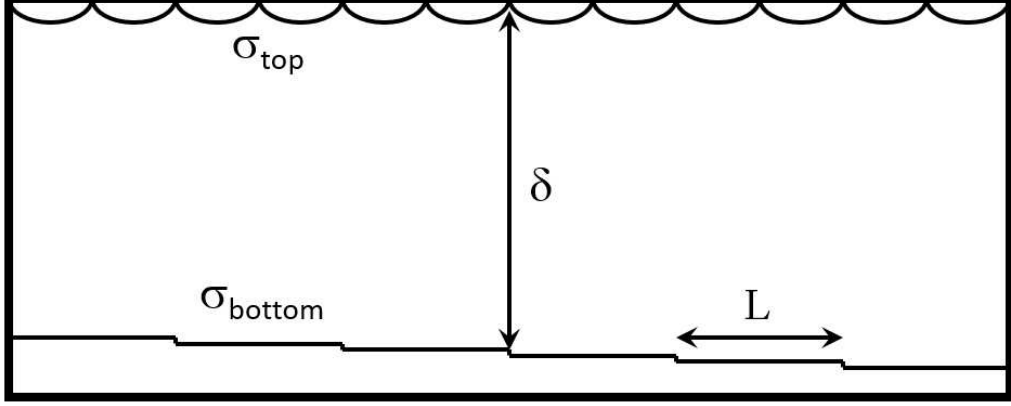


Figure 1: A schematic diagram of an idealized experimental ice growth chamber. The top surface is covered with small ice crystals at a temperature  $T_{top}$ , while the bottom surface at temperature  $T_{bottom}$  supports a faceted basal ice surface with a series of molecular steps separated by a uniform spacing  $L$ . The distance from top to bottom is  $\delta$ , and the supersaturation near the top surface is a constant  $\sigma_{top}$  relative to the bottom ice surface.

where  $a$  is the size of a water molecule and  $\langle v_{basal} \rangle$  is the average perpendicular growth velocity of the faceted surface.

Using a slightly different notation from [1] (defined in detail in [2]), solving the diffusion equation in this simplified one-dimensional geometry gives

$$\frac{c_{sat}}{c_{ice}} D \left[ \frac{\sigma_{top} - \sigma_{bottom}}{\delta} \right] = \langle v_{basal} \rangle = \frac{a}{L} v_{step} \quad (2)$$

which is equivalent to Equation 5 in [1]. As in [1], we estimate  $\delta \approx 200 \mu\text{m}$  as a reasonable model of the idealized system, as this is roughly equal to the size of, and spacing between, the numerous test crystals on the sample surface.

We simplify the analysis slightly relative to [1] by writing  $v_{step}$  as [2]

$$v_{step} \approx \frac{x_s}{a} \alpha v_{kin} \sigma_{bottom} \quad (3)$$

where  $x_s$  is the diffusion length and  $\alpha$  is the attachment coefficient for water molecules striking the ice surface near the step (on the lower terrace), specifically at distances small compared to  $x_s$ . This is essentially equivalent to Equation 7 in [1], but in the limit  $x_s/L \ll 1$ .

At this point our analysis begins to differ substantially from that in [1]. First, we expect that  $\sigma_{top}$  at the top of the idealized box in Figure 1 is much smaller than the supersaturation  $\sigma_{ref}$  calculated at the distant vapor reservoir in the experiment. (In [1],  $\sigma_{ref} = (P_{H_2O}^\infty - P_e)/P_e$ ). Second, we expect that  $\alpha \approx 1$ , compared to the value  $\alpha \approx 10^{-5}$  reported in Figure 10 in [1]. Needless to say, these are large differences in our assumptions pertaining to the same experimental data, which leads us to much different conclusions regarding the surface diffusion length. We proceed by examining these assumptions in more detail.

## 2.1 The near-surface supersaturation

Consider first an estimate of  $\sigma_{top}$ . Our idealized box is quite small, with  $\delta = 200 \mu\text{m}$ , so  $\sigma_{top}$  really represents the supersaturation quite near the test crystals. As described in the Supporting Information associated with [1], the sample surface is several millimeters in size and is covered with a large number of growing ice crystals,

some of which are unobserved, and many of the ice crystals on the sample surface are likely not completely faceted. In addition, the ice crystals making up the vapor reservoir are about 16 mm away from the test crystals, in a test chamber with a somewhat complex geometry. The vapor pressure  $P_{H_2O}^\infty$  defined in [1] is the vapor pressure at the vapor reservoir, which is not the same as the vapor pressure  $\sigma_{top}$  just above the sample surface. The large number of crystals on the sample surface all act as sinks, reducing the vapor pressure relative to  $P_{H_2O}^\infty$ . As stated in [1], “the existence of many crystals and a small amount of nonfaceted faces made precise analysis of a volume diffusion field of water vapor impossibly difficult.” We agree with this statement, and it means that the value of  $\sigma_{top}$  (essentially the value of  $\sigma$  at a height  $\delta$  above a single faceted test crystal surface) is difficult to determine. We would add that the geometry of the test chamber, together with the large number of crystals on the sample surface, suggests that  $\sigma_{top}$  is much smaller than  $\sigma_{ref}$ .

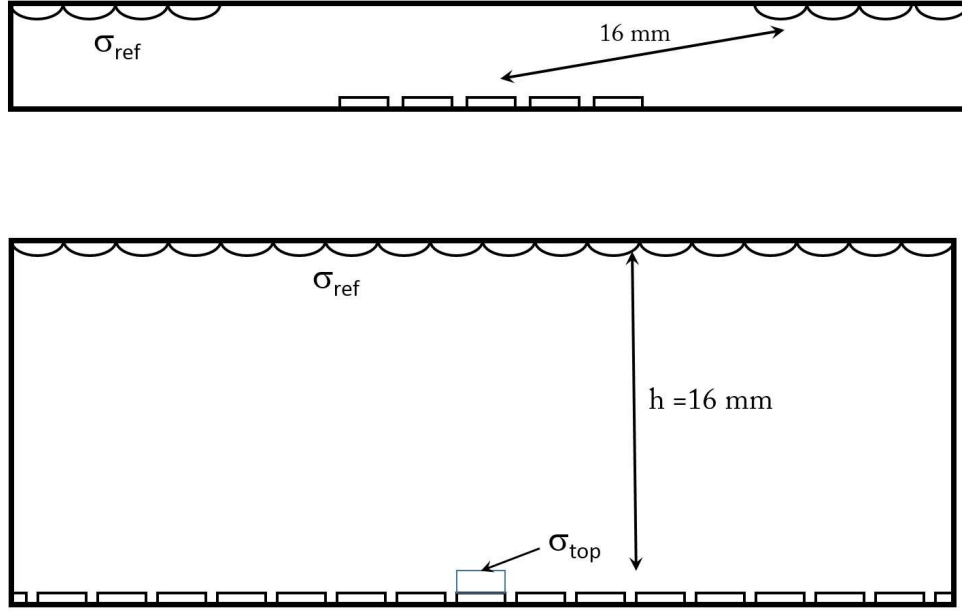


Figure 2: The upper sketch shows a crude schematic approximation of the actual experimental chamber described in detail in the Supporting Information associated with [1]. The sample surface is quite large and contains a large number of ice crystals. The lower sketch is our idealized version of the same chamber, simplified for ease of calculation. Within this large chamber we embed the smaller test chamber in Figure 1, which has  $\sigma_{top}$  on the top surface and a single basal facet on the bottom surface.

We can examine the bulk diffusion problem further by embedding the tiny idealized test chamber in Figure 1 inside a much larger chamber shown in Figure 2, which better represents the actual experimental chamber geometry described in detail in the Supporting Information associated with [1]. For  $h$  we assume a value of 16 mm from [1], so now we see that  $\sigma_{top}$  is essentially the supersaturation just above a large field of growing test crystals. Performing a diffusion analysis similar to that above gives

$$\begin{aligned} \frac{c_{sat}}{c_{ice}} D \left[ \frac{G\sigma_{ref} - \sigma_{top}}{h} \right] &= \langle v_{basal} \rangle \\ &= \langle \alpha_{bottom} \rangle v_{kin} \sigma_{top} \end{aligned} \quad (4)$$

where  $G < 1$  is a correction factor to account for the nontrivial geometry of the test chamber compared to the more open geometry shown in the lower sketch in Figure 2. Also  $\langle \alpha_{bottom} \rangle$  is defined by  $\langle v_{basal} \rangle =$

$\langle \alpha_{bottom} \rangle v_{kin} \sigma_{top}$ , so  $\langle \alpha_{bottom} \rangle$  is essentially the area-averaged attachment coefficient of all the crystals on the sample surface, including nonfaceted areas.

Rearranging Equation 4 gives

$$\sigma_{top} \approx \frac{G \alpha_{diff}}{\langle \alpha_{bottom} \rangle + \alpha_{diff}} \sigma_{ref} \quad (5)$$

where

$$\begin{aligned} \alpha_{diff} &= \frac{X_0}{h} \approx 10^{-5} \\ X_0 &= \frac{D c_{sat}}{v_{kin} c_{ice}} \approx 145 \text{ nm} \end{aligned}$$

In the most likely case that  $\langle \alpha_{bottom} \rangle \gg \alpha_{diff}$  (assuming there are a substantial number of nonfaceted ice crystals on the sample surface, as the authors describe) Equation 5 simplifies to

$$\sigma_{top} \approx \frac{G \alpha_{diff}}{\langle \alpha_{bottom} \rangle} \sigma_{ref} \quad (6)$$

Unfortunately, we have no good way to estimate  $\langle \alpha_{bottom} \rangle$ . In ice-free regions and on perfectly faceted ice surfaces, we expect  $\alpha \approx 0$ , while nonfaceted regions would give  $\alpha \approx 1$ . All growing ice surfaces must contain some molecular steps, and each step contributes to increasing  $\langle \alpha_{bottom} \rangle$ . Assuming a fraction  $10^{-4}$  of  $\alpha \approx 1$  surfaces and  $G \approx 0.1$  gives  $\sigma_{top} \approx 10^{-2} \sigma_{ref}$ , but this is just a very rough estimate. As stated in [1], determining  $\sigma_{top}$  with greater accuracy is “impossibly difficult” without a better defined experimental arrangement. However, our estimate that  $\sigma_{top}$  is much smaller than  $\sigma_{ref}$  is certainly consistent with, and expected from, the experimental details presented in [1].

## 2.2 The attachment coefficient

In [1] the authors mention that their derived values of  $\alpha \approx 10^{-5}$  are much smaller than the values of  $\alpha \approx 0.15$  found in two references. We would add that the measurements in [3] are substantially improved over the older references, giving  $\alpha \approx 1$  on basal surfaces in the absence of a nucleation barrier. We note also that there is no nucleation barrier for molecules impinging near a molecular step. We disagree with the statement in [1] that “there is no value of  $\alpha$  that can be directly compared with ours.” The different experiments are all measuring essentially the same  $\alpha$ , so they can all be compared, and the preponderance of evidence supports  $\alpha \approx 1$ . Moreover, a value of  $\alpha \approx 10^{-5}$  in the absence of a nucleation barrier would imply ice crystal growth velocities that are orders of magnitude below what are commonly observed; the growth of an ordinary snowflake would take weeks with such a low attachment coefficient!

## 3 An Improved Model

Assuming that the above conclusions are essentially correct, we begin with the assumptions that  $\sigma_{top} \ll \sigma_{ref}$  and  $\alpha \approx 1$ , and from these reinterpret the measurements presented in [1]. Going back to the idealized growth chamber in Figure 1, we can rearrange Equations 2 and 3 to obtain

$$v_{step} = \frac{X_0 x_s v_{kin} \sigma_{top}}{a \delta} \left[ \frac{1}{(x_s/L) + (X_0/\alpha \delta)} \right] \quad (7)$$

Taking  $L \rightarrow \infty$  gives the velocity  $v_{isolated-step}$  of an isolated step, and  $v_{step} = v_{isolated-step}/2$  when

$$\frac{x_s}{L_{1/2}} \approx \frac{X_0}{\alpha \delta} \quad (8)$$

Using the 329 Pa data in [1], we take  $L_{1/2} \approx 10 \text{ } \mu\text{m}$  along with our assumptions of  $\delta = 200 \text{ } \mu\text{m}$  and  $\alpha \approx 1$  to obtain  $x_s \approx 10 \text{ nm}$ , 500 times smaller than the  $x_s \approx 5 \text{ } \mu\text{m}$  obtained in [1]. Moreover we see that  $x_s$

depends on  $\delta$ , so there is a substantial uncertainty in our derived  $x_s$  that depends on the uncertainties in our solution of the bulk diffusion equation in the experimental chamber. In a nutshell, the complex geometry of the experimental chamber does not allow a very accurate measure of  $x_s$ , owing to bulk diffusion effects. We estimate that our value of  $x_s \approx 10$  nm is perhaps only accurate to a factor of three.

Because we find  $x_s \ll X_0$ , this means that  $\sigma$  at the ice surface near the growing step is nearly equal to what we called  $\sigma_{bottom}$  above. In other words, bulk diffusion does not substantially lower the supersaturation at the surface of 10-nm features, relative to the supersaturation just above these features. This can be verified to a reasonable approximation using the analytic solution of the diffusion equation for an infinitely long growing cylinder [4]. This verifies Equation 3 above.

### 3.1 A consistency check

To many it seems counterintuitive that covering 0.1 percent of an area with  $\alpha = 1$  surface (0.1 percent because  $x_s/L_{1/2} \approx 10^{-3}$ ), while leaving the remaining 99.9 percent with  $\alpha = 0$ , would reduce the supersaturation  $\sigma_{bottom}$  by a factor of two. To see that this is indeed reasonable, we again rearrange Equations 2 and 3 to obtain

$$\sigma_{bottom} \approx \frac{\alpha_{diff}}{\langle \alpha_{bottom} \rangle + \alpha_{diff}} \sigma_{top} \quad (9)$$

where

$$\alpha_{diff} = \frac{X_0}{\delta} \approx 10^{-3} \quad (10)$$

In the limit of large  $L$  (no molecular steps) we have  $\langle \alpha_{bottom} \rangle = 0$  and  $\sigma_{bottom} \approx \sigma_{top}$ , as expected. But if  $\alpha \approx 1$  surfaces cover just a fraction  $10^{-3}$  of the surface, then  $\langle \alpha_{bottom} \rangle \approx 10^{-3}$  and  $\sigma_{bottom} \approx \sigma_{top}/2$ . Thus even a quite simple diffusion analysis supports our result of  $x_s/L_{1/2} \approx 10^{-3}$ .

### 3.2 A second consistency check

In the limit of large  $L$  in Equation 7, the velocity of an isolated step becomes

$$v_{isolated-step} \approx \frac{x_s}{a} \alpha v_{kin} \sigma_{top} \quad (11)$$

Again using the 329 Pa data in [1], we take  $v_{isolated-step} \approx 12$   $\mu\text{m}/\text{sec}$  along with  $v_{kin} \approx 370$   $\mu\text{m}/\text{s}$  and  $\alpha \approx 1$  to obtain  $\sigma_{top} \approx 10^{-3} \approx 10^{-2} \sigma_{ref}$ , consistent with our rough estimate above.

### 3.3 A third consistency check

We can also consider the case of very low  $\sigma_{ref}$ . With slow growth of the test crystals, one expects essentially all exposed surfaces to become faceted, greatly reducing  $\langle \alpha_{bottom} \rangle$  in Equation 5, to the point that  $\sigma \approx \sigma_{ref}$  throughout the growth chamber. In this case Equation 3 becomes

$$v_{step} \approx \frac{x_s}{a} \alpha v_{kin} \sigma_{ref} \quad (12)$$

so  $\beta^L = v_{step}/\sigma_{ref}$  (defined in [1]) becomes

$$\begin{aligned} \beta^L &\approx \frac{x_s}{a} \alpha v_{kin} \\ &\approx 12000 \text{ } \mu\text{m}/\text{sec} \end{aligned} \quad (13)$$

This is an upper limit, however, since  $\beta^L$  is smaller if  $\langle \alpha_{bottom} \rangle$  is even slightly greater than zero. Thus a small residual  $\langle \alpha_{bottom} \rangle > 0$  in the experiment could easily explain the measured  $\beta^L \approx 700$   $\mu\text{m}/\text{sec}$  presented in [1].

The measured change in  $v_{step}$  with  $\sigma_{ref}$  at higher  $\sigma_{ref}$  (Figure 7 in [1]) can be similarly understood by considering how  $\langle \alpha_{bottom} \rangle$  increases with  $\sigma_{ref}$ . As  $\sigma_{ref}$  increases from zero, the faceted crystals begin to grow,

so steps emerge on their surfaces, increasing  $\langle\alpha_{bottom}\rangle$  and decreasing  $\sigma_{top}$  following Equation 6. Soon the ice growth becomes strongly diffusion limited, resulting in non-flat surfaces with quite large  $\langle\alpha_{bottom}\rangle$ , thus reducing the slope  $dv_{step}/d\sigma_{ref}$  to the degree shown in Figure 7 in [1].

## 4 Conclusions

We have reanalyzed the data presented in [1], and our analysis yields a surface diffusion length  $x_s \approx 10$  nm for water molecules on a basal ice surface at  $T = -8.4$  C. Our analysis assumed  $\alpha \approx 1$  from the outset, a value that is indicated by several other ice growth experiments, while we rejected the extraordinarily low value  $\alpha \approx 10^{-5}$  reported in [1]. Essentially all of the data presented in [1] can be explained in a reasonable and self-consistent way using our model, as described above. Moreover, our model does not distinguish whether ad molecules are attaching to the step from the upper or lower terrace, or both. Thus we find that the step velocity measurements provide no useful information about the height of the Ehrlich-Schwoebel barrier, contrary to what was concluded in [1].

It has long been known, and was recently demonstrated with improved accuracy in [3], that growing small, isolated, faceted crystals in a near-vacuum environment reduces the effects of bulk diffusion to much more manageable levels, thus better revealing molecular kinetic effects. Measuring the growth velocities of one-molecule-high steps in such an experimental system would be a welcome next step toward understanding the fundamental physics of ice growth dynamics.

## References

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